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DOCUMENT-IDENTIFIER: US 5059327 A
TITLE: Cross-linked separation membrane and process for pervaporation

Brief Summary Text (6):
For example, regarding separation of an aqueous ethanol solution, U.S. Pat. No. 2,953,502 discloses a cellulose acetate homogeneous membrane and U.S. Pat. No. 3,035,060 discloses a polyvinyl alcohol membrane. However, both membranes have low separation factors. Although Japanese Patent Kokai No. 59-109204 discloses a composite membrane having a cellulose acetate membrane or a polyvinyl alcohol membrane as a skin layer and Japanese Patent Kokai No. 59-55305 discloses a polyethylene imine crosslinked composite membrane, their permeation rates or separation factors are low. In Japanese Patent Kokai No. 60-129104, there is described a membrane comprising an anionic polysaccharide. However, the material used for the membrane described in the Examples of this literature is a water soluble polymer and therefore durability of the membrane against an aqueous solution containing a low concentration of an organic compound is inferior. Then, in this literature, there is also described that the membrane is subjected to a crosslinking treatment with a sufficient amount of a crosslinking agent to render the membrane essentially insoluble in water, although it is not disclosed in the Examples thereof. However, usually, when a crosslinking treatment is effected, a permeation rate is decreased, while a separation factor is increased as shown by Comparative Examples hereinafter. In German Patent No. 3220570, although there is disclosed that a composite membrane obtained by coating a polymer of polyvinyl alcohol crosslinked with maleic acid on a polyacrylonitrile porous membrane shows very high separability, the permeation rate thereof is very low.

Drawing Description Text (2):
FIG. 1 is an infrared absorption spectrum of one embodiment of a separation membrane according to the present invention before subjecting it to heat treatment for crosslinking.

Drawing Description Text (3):
FIG. 2 is an infrared absorption spectrum of the separation membrane of FIG. 1 after subjecting it to heat treatment at 120.degree. C. for 2 hours to effect crosslinking.

Detailed Description Text (12):
The diffusion rate is determined by shape, size and an agglomeration state of permeate molecules, and a free volume of a membrane. In order to increase a separation factor .alpha..sub.AB, shape of permeate molecules in a feed mixture should be largely different. In general, a smaller molecule has a larger diffusion rate. However, when a given material to be separated is fixed, it is difficult to increase a diffusion rate .alpha..sub.AB by difference in shape of permeate molecules. On the other hand, a free volume of a membrane is defined by molecular spacings in the sense of a molecular measure, although it is not macroscopic holes. When a low molecular weight material which makes molecular motion of a high molecular weight material vigorous is contained, a free volume of a membrane becomes larger, which facilitates permeation. In a membrane having a larger free volume, difference between diffusion rates due to difference in size of permeate molecules becomes smaller, whereas, in a membrane having a smaller free volume, difference between diffusion rates due to difference in size of permeate molecules becomes larger. In order to increase a separation factor by utilizing size of permeate

molecules, a free volume of a membrane should be small. In order to make a free volume of a membrane smaller, there is employed such a method as introduction of a crosslinking structure or crystalline structure to form three dimensional network.

Detailed Description Text (13):
According to the present inventor's study on various membranes for separation of an aqueous solution containing a water soluble organic compound, particularly, ethanol by pervaporation, it has been found that a separation membrane which is obtained by adding polystyrene sulfonic acid to polyvinyl alcohol having a large solubility parameter, i.e., strong hydrophilic nature, and subjecting the mixture to heat treatment to effect intermolecular crosslinking reaction between the hydroxy group of polyvinyl alcohol and the sulfonic acid group of polystyrene sulfonic acid can selectively separate the alcohol from the water-alcohol mixture, and the membrane has sufficient durability as well as high permeation rate and separation factor throughout a wide concentration range of the alcohol. The sulfonic acid group of the above reaction mixture may be introduced as a sulfonate group.

Detailed Description Text (15):
The separation membrane of the present invention can be prepared by, for example, dissolving polyvinyl alcohol or the polyvinyl alcohol copolymer, and polystyrene sulfonic acid or the polystyrene sulfonic acid copolymer in water or an aqueous solution containing a water soluble organic compound such as an alcohol or the like and casting the solution on a porous supporting material, for example, an ultrafiltration membrane. Drying and heat treatment are carried out, simultaneously to effect intermolecular crosslinking to form a coat layer on the porous supporting material a crosslinked reaction mixture of the polyvinyl alcohol or polyvinyl alcohol copolymer and the polystyrene sulfonic acid or polystyrene sulfonic acid copolymer. The heat treatment is carried out at a temperature in the range of 80.degree. to 200.degree. C., preferably, 100.degree. to 150.degree. C. The mixing ratio of polyvinyl alcohol and polystyrene sulfonic acid is in the range of, preferably, 1 to 10 parts by weight, more preferably, 1.5 to 5 parts by weight of polyvinyl alcohol per 1 part by weight of polystyrene sulfonic acid.

Detailed Description Text (18):
In the membrane thus produced, OH group of polyvinyl alcohol and SO.sub.3 H group of polystyrene sulfonic acid are reacted to form intermolecular crosslinking. Formation of crosslinking can be confirmed by solubility of the membrane in a mixture to be separated or the infrared absorption spectrum of the membrane. When crosslinking is not formed, the membrane is dissolved during separation operation. A partially remaining sulfonic acid group is neutralized with a base to convert into a sulfonate. Examples of the counter cation of the sulfonate include alkali metals, alkaline earth metals, transition metals and ammonium ions of the formula R.sub.4 N.sup.+ wherein R is hydrogen or alkyl. Preferably, it is an alkali metal, particularly, sodium.

Detailed Description Text (31):
Polystyrene having a polymerization degree of 1,000 to 1,400 (10 g) was dissolved in carbon tetrachloride (200 ml) at 60.degree. C. for 1 hour. Then, the solution was placed in a four necked flask and conc. sulfuric acid (30 ml) was added to the flask under nitrogen atmosphere. The mixture was reacted at 60.degree. C. for 4 hours. The reaction mixture was added to dehydrated ether to form a white precipitate. To the precipitate was added carbon tetrachloride to dissolve the precipitate. The solution was further added to dehydrated ether to form a precipitate. This procedure was repeated four times to purify the reaction product. The reaction product was confirmed as polystyrene sulfonic acid by its infrared absorption spectrum. To the polystyrene sulfonic acid thus obtained (1.2 g) were added polyvinyl alcohol having a polymerization degree of 2,000 (1.8 g), ethanol (1.4 g) and water (24 g) and the mixture was dissolved at 80.degree. C. The solution was applied on an ultrafiltration membrane composed of polyacrylonitrile with a spin coating machine (800 r.p.m.). The coated membrane was dried at 40.degree. C. for 1 hour and then subjected to heat treatment at 120.degree. C. for 2 hours to effect crosslinking. The pervaporation ability in aqueous 95% (w/w) ethanol solution of the membrane thus obtained was such that the permeation rate was 3.8.times.10.sup.-2 kg/m.sup.2. hr and the separation factor (.alpha..sub.EtOH.sup.H.sbsp.2.sup.O) was 97.

Detailed Description Text (33):
Polystyrene having a polymerization degree of 1,000 to 1,400 (10 g) was dissolved in carbon tetrachloride (200 ml) at 60.degree. C. for 1 hour. Then, the solution was placed in a four necked flask and conc. sulfuric acid (30 ml) was added to the flask under nitrogen atmosphere. The mixture was reacted at 60.degree. C. for 4 hours. The reaction mixture was added to dehydrated ether and to form a white precipitate. To the precipitate was added carbon tetrachloride to dissolve the precipitate. The solution was further added to dehydrated ether to form a precipitate. This procedure was repeated four times to purify the reaction product. The reaction product was confirmed as polystyrene sulfonic acid by its infrared absorption spectrum. To the polystyrene sulfonic acid thus obtained (1.2 g) were added polyvinyl alcohol having a polymerization degree of 2,000 (1.8 g), ethanol (14 g) and water (24 g) and the mixture was dissolved at 80.degree. C. The solution was applied on an ultrafiltration membrane composed of polyacrylonitrile by a spin coating machine (800 r.p.m.). The coated membrane was dried at 40.degree. C. for 1 hour and then subjected to heat treatment at 120.degree. C. for 2 hours to effect crosslinking.

Detailed Description Text (38):
The ion exchange resin was filtered off and to the filtrate (50 ml) were added polyvinyl alcohol (4.2 g) and water (50 g). The solution was applied on a polyacrylonitrile ultrafiltration membrane by a bar coating machine. The coated ultrafiltration membrane was dried at 40.degree. C. for 1 hour and subjected to heat treatment at 120.degree. C. for 2 hours to effect intermolecular crosslinking. The pervaporation ability of this membrane is shown in Table 2.

Detailed Description Text (46):
As shown by these drawings, absorption bands at 1180 cm.sup.-1 and 1450 cm.sup.-1 are newly appeared by heat treatment at 120.degree. C. for 2 hours. These absorption bands are corresponding to R--O--SO.sub.2 --R formed by the crosslinking reaction of the polyvinyl alcohol and polystyrene sulfonic acid, and become more intense by heating for a longer time.

Current US Cross Reference Classification (9):
210/500.42

CLAIMS:

4. A membrane according to claim 1, wherein the membrane is obtained by applying a mixture of polyvinyl alcohol and polystyrene sulfonic acid on a porous supporting material and then subjecting the mixture to a crosslinking treatment.

6. A membrane according to claim 4, wherein the crosslinking treatment is effected by heating at 100.degree. to 150.degree. C.